IMPULSE RESISTANCE SINTERING OF TUNGSTEN

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MATERIALS APPLICATION DIVISION

September 1976

ARMY MATERIALS AND MECHANICS RESEARCH CENTER
Watertown, Massachusetts 02172

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AMMRC TR 76-32	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) IMPULSE RESISTANCE SINTERING OF TUNGSTEN		5. TYPE OF REPORT & PERIOD COVERED Final Report 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Jacob Greenspan		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Army Materials and Mechanics Research Center Watertown, Massachusetts 02172 DRXMR-K		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS D/A Project: 1T162105AH84 AMCMS Code: 612105.11.H8400
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Materiel Development and Readiness Command, Alexandria, Virginia 22333		12. REPORT DATE September 1976 13. NUMBER OF PAGES 13
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Presented at the AMPF Meeting, Frankford Arsenal, October 1975.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Tungsten
Sintering
Powder metallurgy

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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ABSTRACT

Applicability of impulse resistance sintering to tungsten, and to powder mixes rich in tungsten, was explored in experiments relating process parameters to the sample characteristics. Short consolidation time, fine microstructure, and the ability to handle unusual alloy combinations are some characteristics unique to the method.

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INTRODUCTION

The method of "impulse resistance sintering" is capable of applying high heat and simultaneous pressure to a powder compact, and for this reason should be effective in consolidating refractory metal powders. The present work explores some avenues of this kind in the area of tungsten powder metallurgy. Several interesting developments are reported.

BACKGROUND

Impluse resistance sintering is a modification of the process known as "spark sintering", which in turn was an outgrowth of the much earlier "electric resistance sintering" process. All are electromechanical in nature, employing pressing rams as electrodes that transmit electric current through a powder compact. In this way the compact is subjected to heat and pressure simultaneously. However, the processes differ in some detail in the way by which the powder particles are heated. In electric resistance sintering, heat is generated explicitly by the internal or bulk electric resistance of the powder particles, and heat distribution is relatively uniform. This method employs direct current only. In spark sintering, electric sparking is introduced at a multitide of interparticle contact points, concentrating the heat at particle surfaces. When the sparking is terminated the usual resistance mode takes place. The method incorporates an alternating current with the basic direct current. In impulse resistance sintering, a similar heating mode is sought by means of interparticle contact resistance, employing direct current only.

Electric resistance sintering was introduced and patented in 1933 by Taylor.[1] Some developments in utilization that followed were by Jones in 1940,[2] Cremer in 1944,[3] and Ross in 1945.[4] It was recognized early that the relatively short time for sintering by this method, as compared with furnace sintering methods, could be important with respect to the metallurgical time-temperature-transformation phenomena and impurity pickup. For example, in 1955 Lenel[5] indicated that carbon embrittlement of the binding phase in a cemented carbide composite could be minimized in this way.

Spark sintering was introduced and patented in 1962 and 1966 by Inoue[6] and has since been applied in an exploratory way to a number of materials.[7,8] A demonstrated advantage was its use in a closed die pressing approach to obtain near net component shapes in relatively complex beryllium shapes. Also, the mechanical properties were reported to have been affected in a favorable way for

1. TAYLOR, G. F. *Apparatus for Making Hard Metal Compositions.* U.S. Patent 1,896,854, February 1933.
2. JONES, W. D. *The Metal Industry.* March 1944, p. 225.
3. CREMER, G. D. *Powder Metallurgy.* U.S. Patent 2,355,954, August 1944.
4. ROSS, W. D. *Method and Apparatus for Making Solid Objects from Metal Powders.* U.S. Patent 2,372,605, March 1945.
5. LENEL, F. V. *Resistance Sintering Under Pressure.* Journal of Metals, January 1955, p. 158-167.
6. INOUE, K. *Electric Discharge Sintering.* U.S. Patent 3,241,956, March 1962, and U.S. Patent 3,250,892, May 1966.
7. BOESEL, R. W., JACOBSON, M. I., and YOSKIOKA, I. S. *Spark Sintering Tames Exotic P. M. Materials.* Materials Engineering, October 1969.
8. BOESEL, R. W. *Spark Sintering, An Unusual Method.* Met. Prog., v. 99, 1971, p. 74.

beryllium and for Ti-6Al-4V by Goetzel and DeMarchi,[9] presumably as a result of short sintering time. However, difficulty in attaining cost effectiveness in the manufacture of certain Naval Ordnance components using conventional alloys is indicated in Reference 10. This was related in part to mold wear, lack of uniformity, and lack of reproducibility, normally cost-effective factors in most processes.

In application to less conventional materials, a silicon carbide-aluminum matrix composite for armor was consolidated effectively by impulse resistance sintering by Hull and Daniels[11] in 1971. This was an example of liquid phase sintering. In 1972, Shepard and Croft[12] obtained a high integrity TiB for armor by impulse resistance sintering, a powder mixture of TiB_2 and Ti, incorporating the chemical combination with the sintering process. This approach was studied further by Isserow[13] in 1973. Based on these demonstrated aspects of versatility, applicability of the process to tungsten powder mixtures was explored in this investigation.

EQUIPMENT, MATERIALS, AND PROCEDURES

The basic elements of the equipment were a power supply (Figure 1), and a hydraulic press and control console (Figure 2). The power supply consisted of a bank of dc generators, connected in parallel, having a capacity of 600 kW, and able to generate 10,000 amperes. Bus bars running from the power supply to a pair of water-cooled copper electrode base plates were attached to but insulated from the upper and lower plates of the press. A series of switches in the control console provided stepwise control of the power input to this point.

A graphite die-and-ram assembly such as that illustrated in Figure 3 was positioned between the above-base plates. The ram geometry was designed to minimize the conductive heat loss and to maximize passage of the electric current through the compact. Vertical displacement of the platen during the pressing operation was instrumented for autographic recording, which provided an indication of the course of consolidation of the powder compact. Temperature, sensed by the thermocouple shown in Figure 3, also was autographically recorded. All recorders were activated by a main contactor switch.

The tungsten powders used were of -10 micron particle size, derived by hydrogen reduction, available as a standard grade commercial product. The nickel, aluminum and titanium powders, employed as additives, were of -5 micron particle size. Purity was of the order of 99.5%.

9. GOETZEL, C. G., and DeMARCHI, V. S. *Electrically Activated Pressure Sintering of Titanium Powders.* Powder Metallurgy International, v. 3, 1971, p. 80-87 and 134-136.
10. *Spark Sintering of Powdered Metal,* Naval Ordnance Station, Louisville, Kentucky, Report MT-021, June 1974.
11. HULL, J. L., and DANIELS, N. M. G. *Improved Composite Armor Produced by Impulse Resistance Sintering.* Stanford Research Institute, Contract DAAG 46-70-C-0019, Final Report, AMMRC CR 71-20. October 1971.
12. SHEPARD, L. A., and CROFT, W. J. *Impulse Resistance Sintering.* Army Materials and Mechanics Research Center, AMMRC TR 72-37, December 1972.
13. ISSEROW, S. *Impulse Resistance Sintering of Compounds for Armor Applications.* Army Materials and Mechanics Research Center, AMMRC TR 73-43, September 1973.

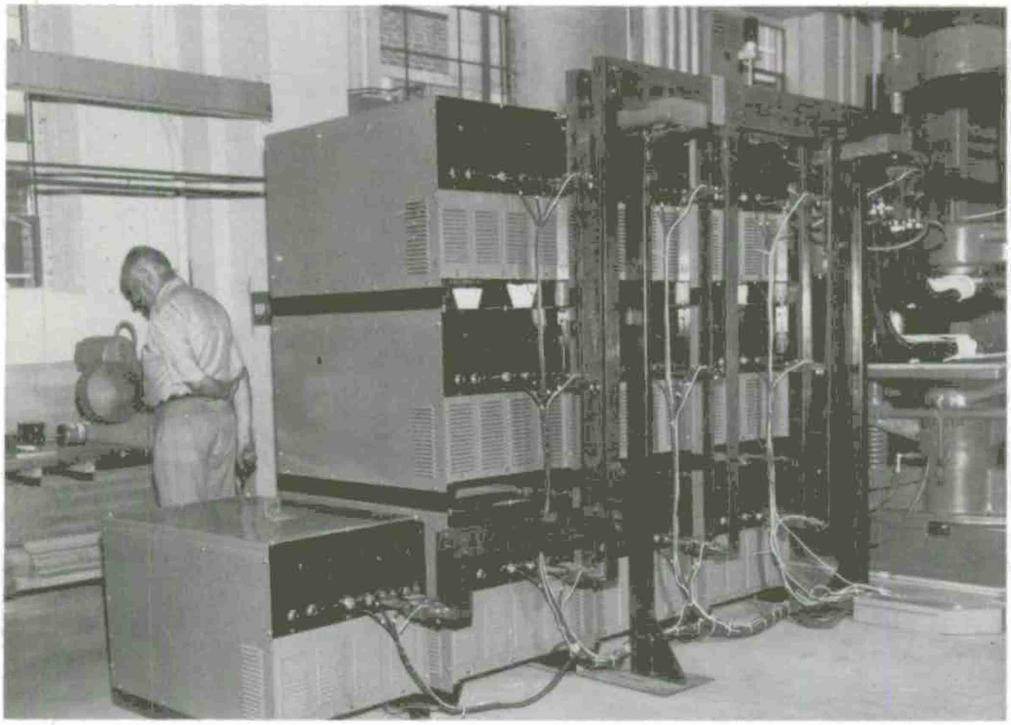

Figure 1. Generator bank for impulse resistance sintering.
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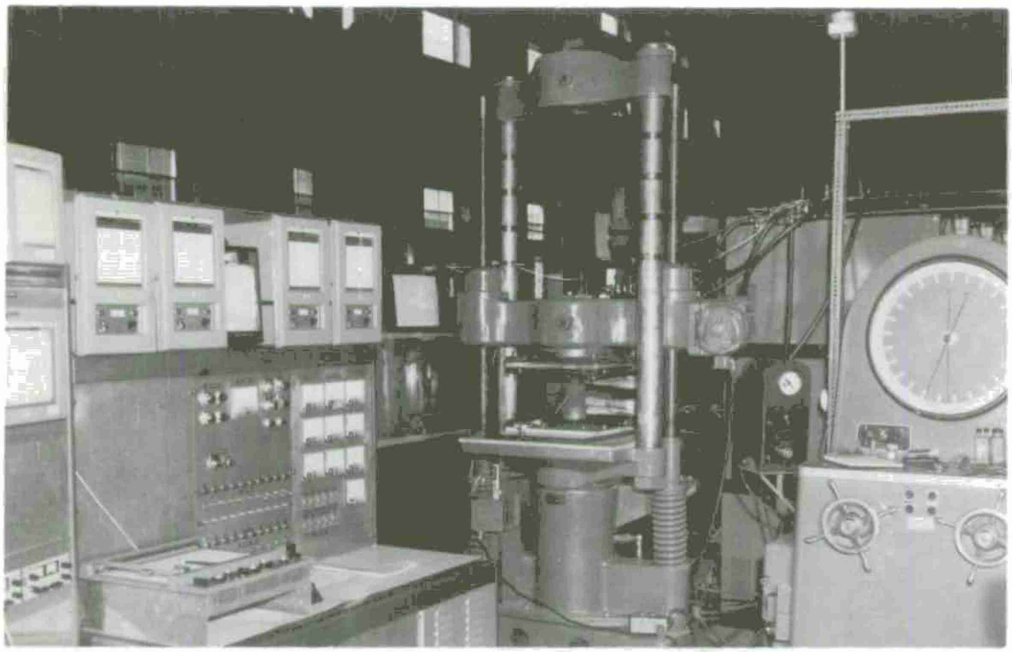

Figure 2. Control console and hydraulic press for impluse resistance sintering.
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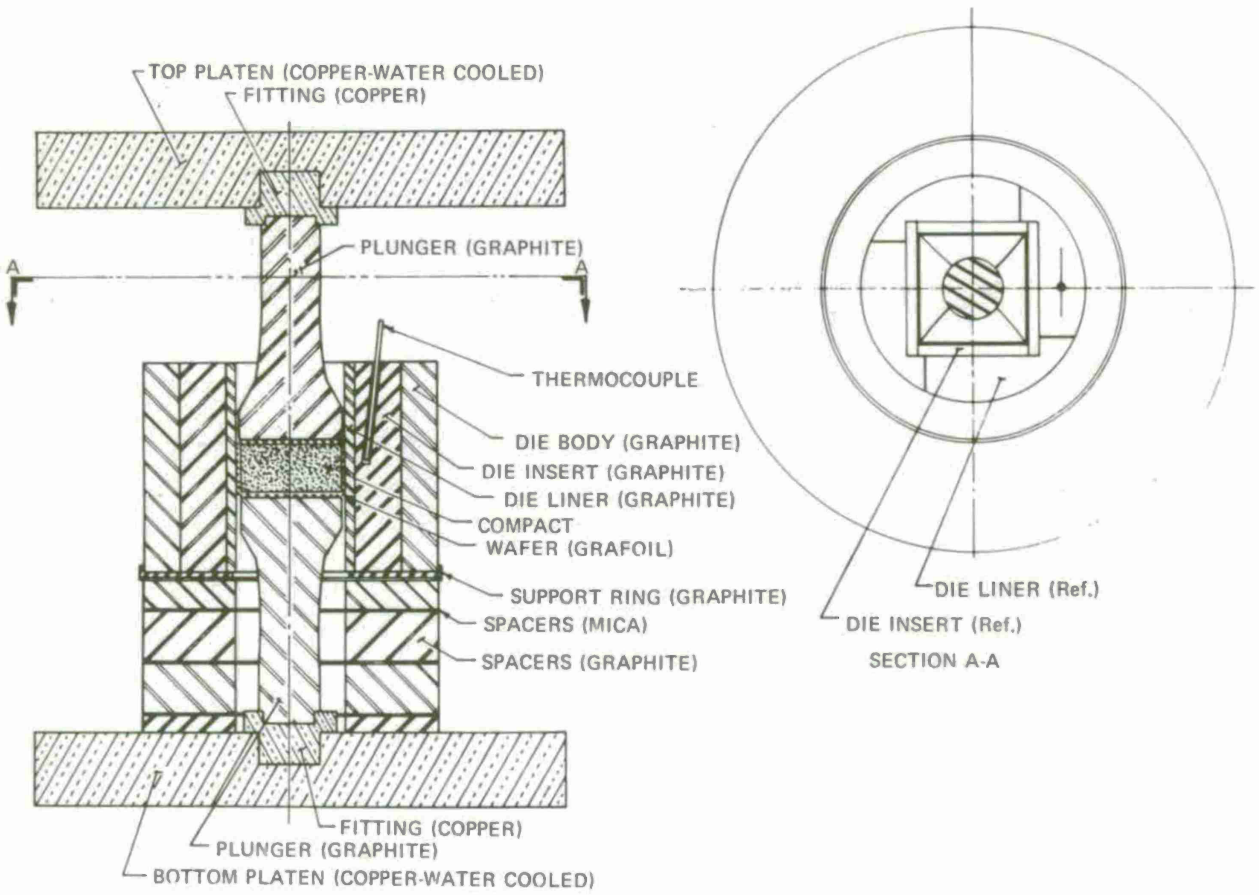

Figure 3. Die, ram and accessories for impulse resistance sintering.

With powders packed at about 40% density, the die assembly, Figure 3, was positioned between the electrode base plates. A flow of argon gas was introduced around the assembly to minimize erosion of the die and oxidation of the charge. With relatively low initial ram pressure of the order of 1000 psi applied to induce the desired high interparticle contact resistance, the current was applied in a single surge, held until a plateau in consolidation was reached, and then the pressure was increased to 2000 psi for additional consolidation to an indicated end point in ram movement. Alternatively, a ram pressure of 2000 psi was used throughout. The cycle was then terminated and the compact allowed to cool in place under pressure. Experimental samples were of the order of 3 inches long and 1/2-inch-square cross section and were consolidated within a time period of the order of 6 to 10 minutes. The degree of consolidation, the microstructures, and in some cases the flexural strength of the as-pressed bars are discussed in the following.

RESULTS

Tungsten powders were consolidated in accordance with the parameters shown in Table 1 and Figure 4. Sintered densities of the order of 62% to 65% were obtained with current densities in the range of 2700 to 3500 amperes per square

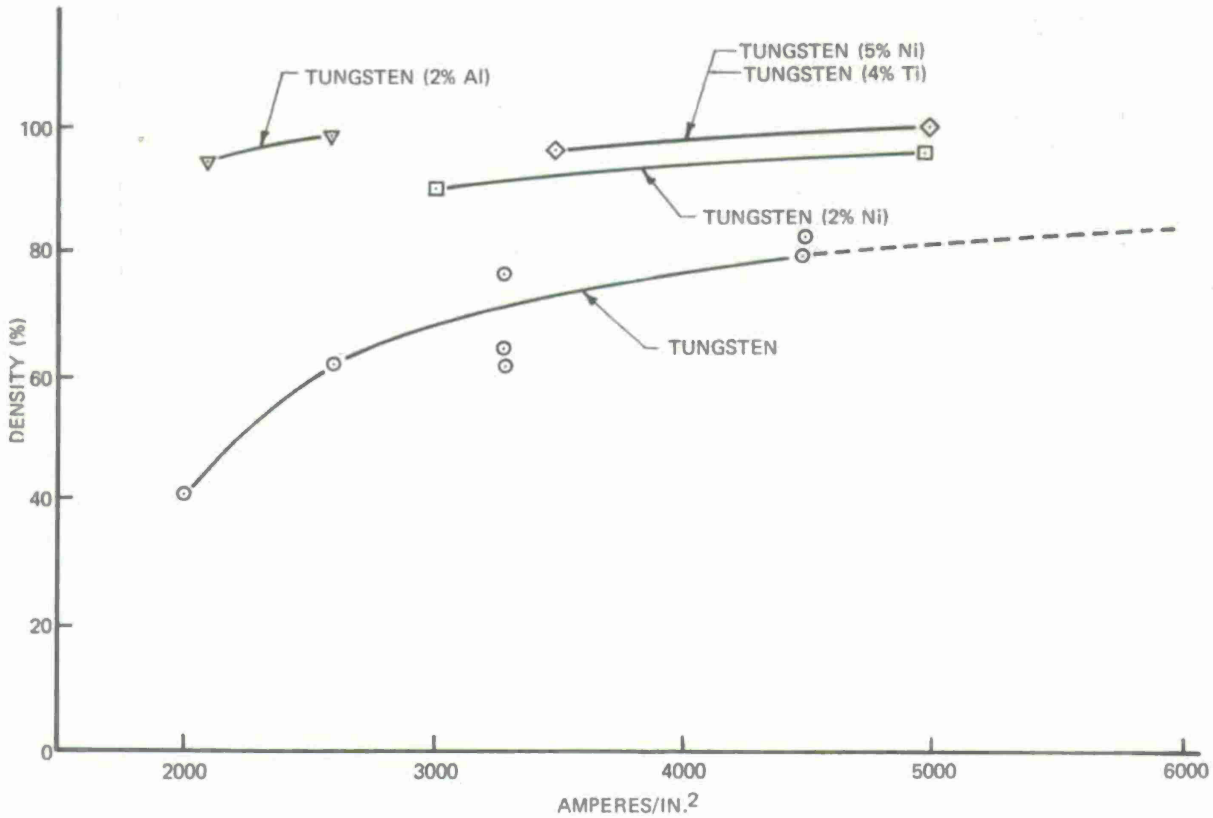

Figure 4. Densification of impulse resistance sintered powders.

Table 1. IMPULSE RESISTANCE SINTERING OF TUNGSTEN POWDERS*

Mark	Current Density Ampere inch^2	Pressure (ksi) On Compact Initial	Final	Sample Density g/cm^3	%	Flexural Strength ksi
1	2000	750	2000	8.2	43	8.1
2	2730	750	2000	11.8	62	-
3	2730	1000	2000	12.3	64.5	-
4	3400	1000	2000	12.0	63	-
5	3470	1000	2000	11.8	62	21
6	3470	1000	2000	12.1	64	-
7	4735	1000	2000	15.0	78	28.2
8	4735	1000	2000	14.8	76	-

*Particle size: -10 microns
Green density: 40%
Sample size, compacted: 3"L x 1/2" x 1/2"
Time, IRS cycle: 6 minutes

inch. With current density increased to 4700 to 5000 amperes per square inch, the degree of consolidation was increased to 76% to 78%. In view of the relatively large volume fraction of pores, illustrated in Figure 5, the flexural strengths of as-sintered bars, as shown in Table 1, are indicative of an effective degree of particle joining or sintering at interparticle contact points. Therefore, it is likely that very high local temperatures, as desired, were generated at these points during early stages of consolidation. However, the

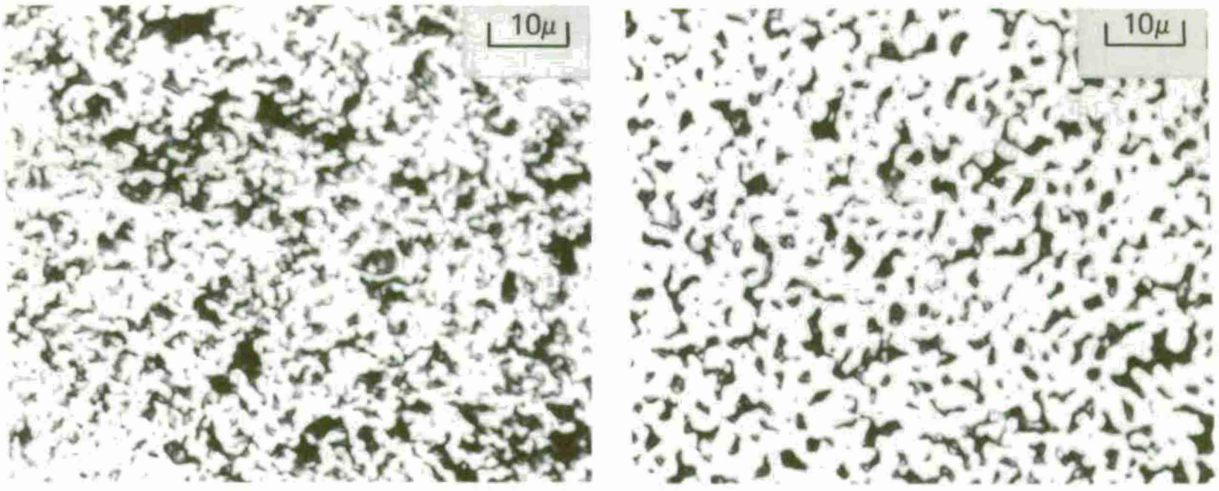

Figure 5. Impulse resistance sintered tungsten powder showing large volume fraction of pores.
a. 64% dense b. 74% dense

leveling of these consolidation curves at approximately 80%, Figure 4, shows the insufficiency of the follow-on temperature-pressure parameters of the processing in this case.

The influence of aluminum additions was to shift the consolidation curve upward as shown in Figure 4. Table 2a shows that with 1% aluminum addition, sintered densities of 96% to 98% were obtained using current densities of 2400 to 3700 amperes per square inch. With 2% aluminum, essentially full consolidation was achieved using 2400 amperes per square inch. Photomicrographs in Figure 6 show equiaxed grain structure and grain diameters about equal to those of the initial powder particles. It is presumed, therefore, that the structure may simply be that of compacted particles, or it may be one of recrystallization and grain growth in spite of the relatively short heat cycle. The microstructure also shows an indication of coalescence and squeeze-out of the aluminum.

Titanium additions shifted the consolidation curves upward as shown in Figure 4. Table 2b shows that for mixtures containing 1% titanium, sintered density of about 82% was obtained using 2400 to 2700 amperes per square inch. This was increased to about 92% by increasing the current density to about 5000 amperes per square inch. At this current density, a 2% titanium mixture was consolidated to about 94% density, whereas a 4% titanium mixture was consolidated to 97% to 100% density. Figure 7 shows very fine grain sizes, of the order of one micron diameter in some cases. Titanium particles do not appear to have coalesced, as did the aluminum, though it is believed that these particles were fully molten during compaction. Reaction between titanium and tungsten constituents is evident, and it is believed that the very fine grain structure is the result of crystallization and early growth of a W-Ti binary phase.

Nickel additions also shifted the consolidation curve upward as shown in Figure 4. Table 2c shows 92% density for a 1% nickel mixture, 96% to 97.5% density for mixtures of 2% to 4% Ni, and essentially full density for 5% nickel when employing 5000 amperes per square inch. With less current density, lesser

Table 2. IMPULSE RESISTANCE SINTERING OF BLENDED POWDERS OF TUNGSTEN

Additive, %	Current Density Amp/In.^{2}	Time Min.	Sample Density: Calculated Theoretical g/cm^3	Sample Density: Measured g/cm^3	%	Flexural Strength ksi
a. Aluminum, 2	2400	6	16.95	17.2	100*	-
2				17.4	100*	-
1			17.91	17.6	98	-
1				17.5	97.6	-
1	3735			17.2	96	57.7
1				17.6	98	-
1				17.6	98	-
1				17.6	98	66.58
b. Titanium, 1	2400	12	18.4	15.0	82	-
1	2666	6		14.8	82	-
1	4400	6		16.0	87	-
1	4735	10		16.4	89	46.8
2	4735	10	17.85	16.8	94	-
4	4735	10	16.83	16.4	97.5	62.1
1	5000	10	18.4	17	92.4	-
1		10		16.9	92.4	-
4		6	16.83	16.9	100	-
4		6		16.3	97	-
c. Nickel, 2	2700	11	18.57	15.6	84	-
2	5000	11		17.8	96	-
4		11	18.17	17.4	96	-
2.5		6	18.48	18	97.4	-
1		5	18.78	17.3	92	-
5		5	17.98	18.2	100†	71.4
5		6		18.2	100†	-
5		5		17.7	98.4	-
5		5		18.3	100†	-
5	3400	6		17.4	97	-

Note: Particle size: Tungsten -10 micron; additive -5 micron
Green density: 40%
Sample size, compacted: 3"L x 1/2" x 1/2"
Pressure on compacts: Al - 1500 psi, Ti and Ni - 2000 psi

*Indicates squeeze-out of liquid aluminum
†Indicates squeeze-out of nickel

degrees of compaction were obtained. Thus when 2700 amperes per square inch was employed on a 2% Ni compact and 3400 amperes per square inch on a 5% Ni compact, the corresponding densities were 84% and 97% of the calculated theoretical values. Photomicrographs in Figure 8 show a two-phase metwork structure. With 4% nickel the network is continuous, but with 2% nickel there is some abutment of tungsten particles. The structures are seen to contain some degree of porosity in these instances which correspond to 96% of the calculated theoretical densities.

SUMMARY, CONCLUSIONS, AND REMARKS

It appears significant that the alloy combinations W-Al and W-Ti, which normally do not occur within the current tungsten alloy technology, are readily synthesized by the present impulse resistance sintering approach. Tungsten-aluminum fully consolidated, shown in Figure 6b, exhibits equiaxed grains of the order of 10 microns diameter. Tungsten-titanium structures of low porosity shown

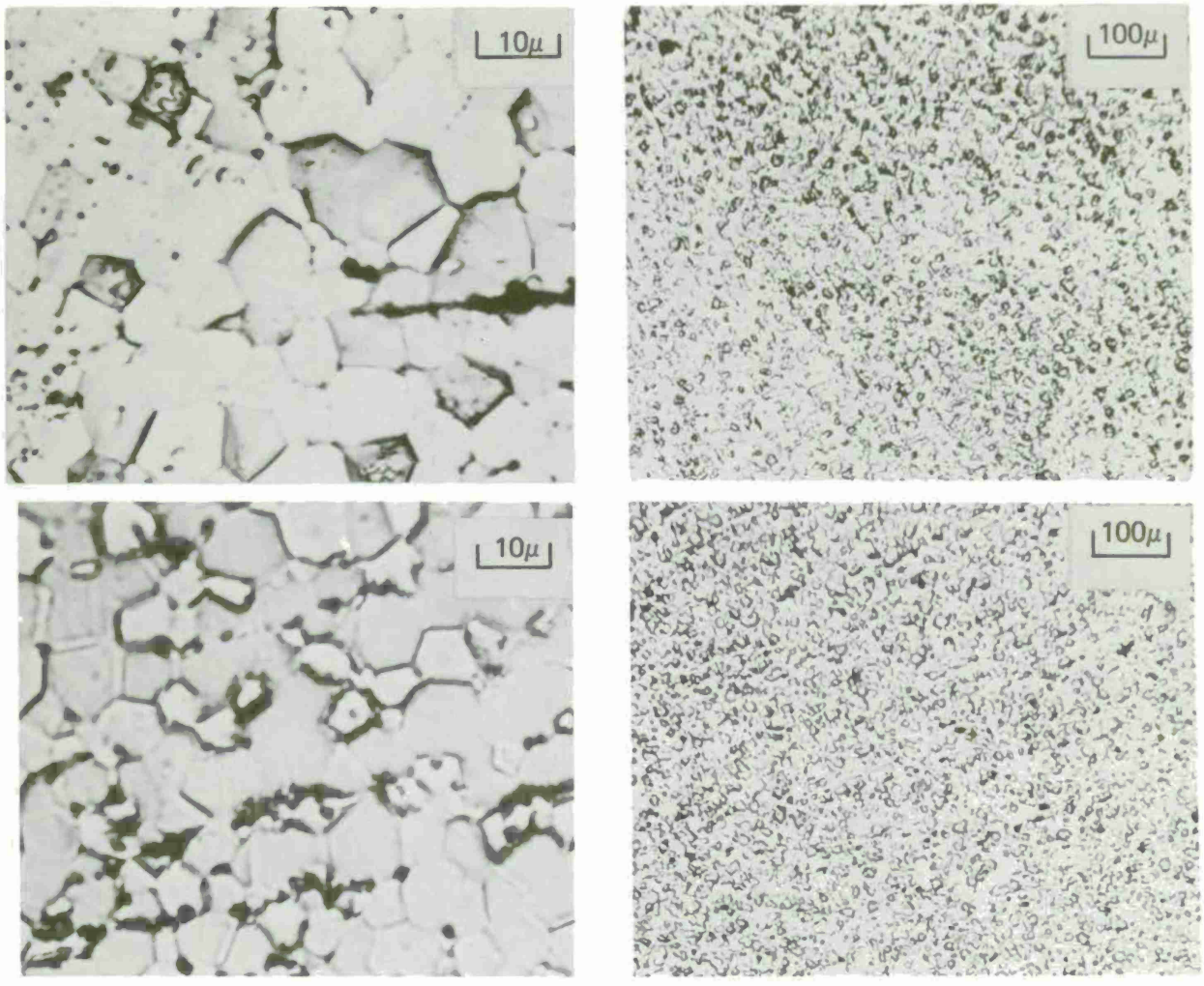

Figure 6. Impulse resistance sintered tungsten-aluminum powder mix.
a. 99% W-1% Al - 98% dense.
b. 98% W-2% Al - 100% dense.

in Figure 7 exhibit grain diameter an order of magnitude finer. It appears significant that the network structures common to W-Ni type alloys processed by furnace sintering methods also are formed by the present impulse resistance sintering approach, as shown in Figure 8a.

The temperature-pressure parameters of the present approach were not sufficient to consolidate tungsten powders beyond approximately 80% density. The influence of the intermixed Al, Ti, and Ni powders was to shift the consolidation curve upward, under the circumstances shown in Figure 4, to obtain nearly complete consolidation. In all cases the upward shift was coincident with the presence of relatively small quantities of liquid phase, which seems to affect the mechanics of particle movement in a favorable way. Sintered density up to 18.3 g/cm^3 was demonstrated for a W-Ni mixture.

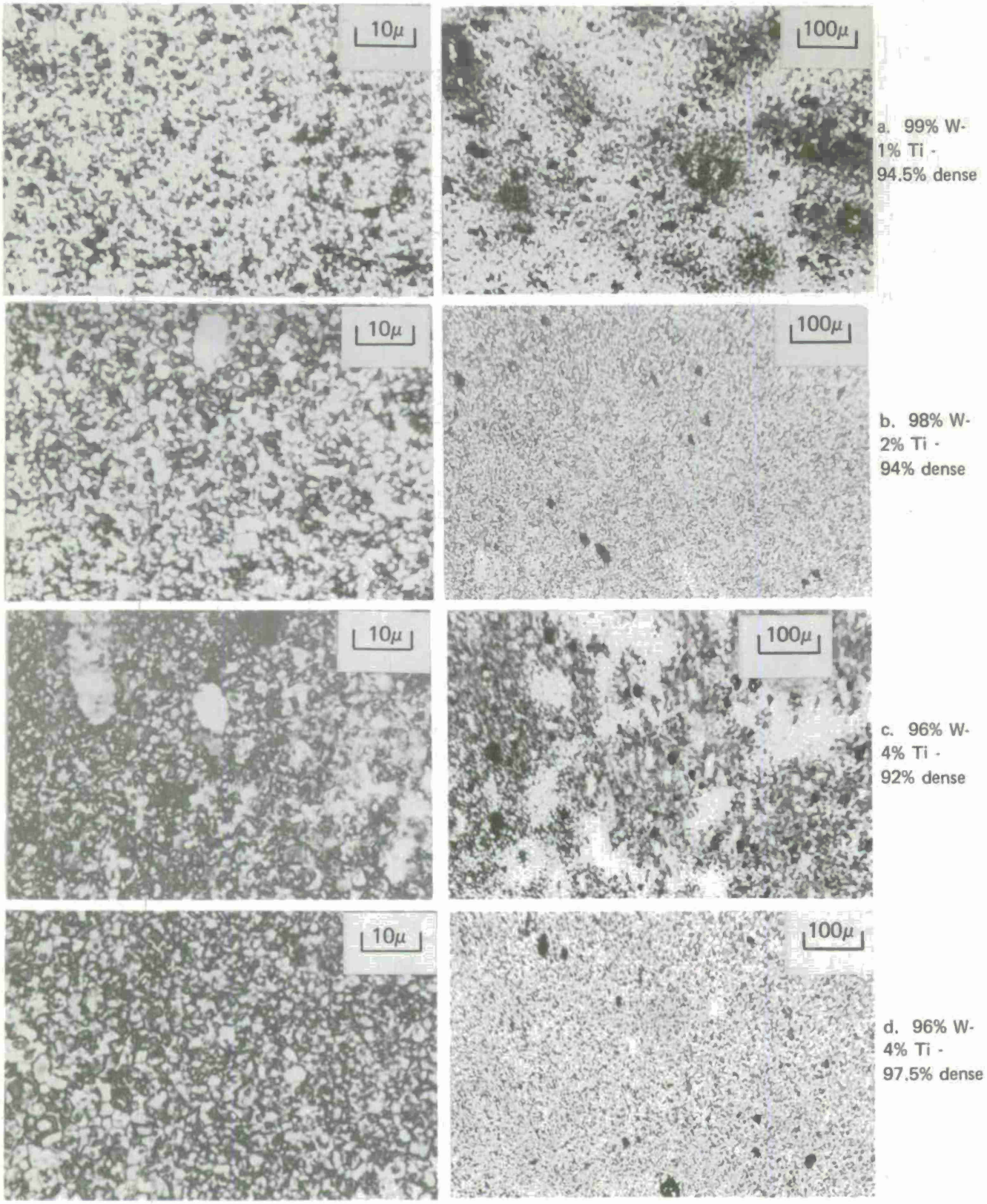

Figure 7. Impulse resistance sintered tungsten-titanium powder mix.

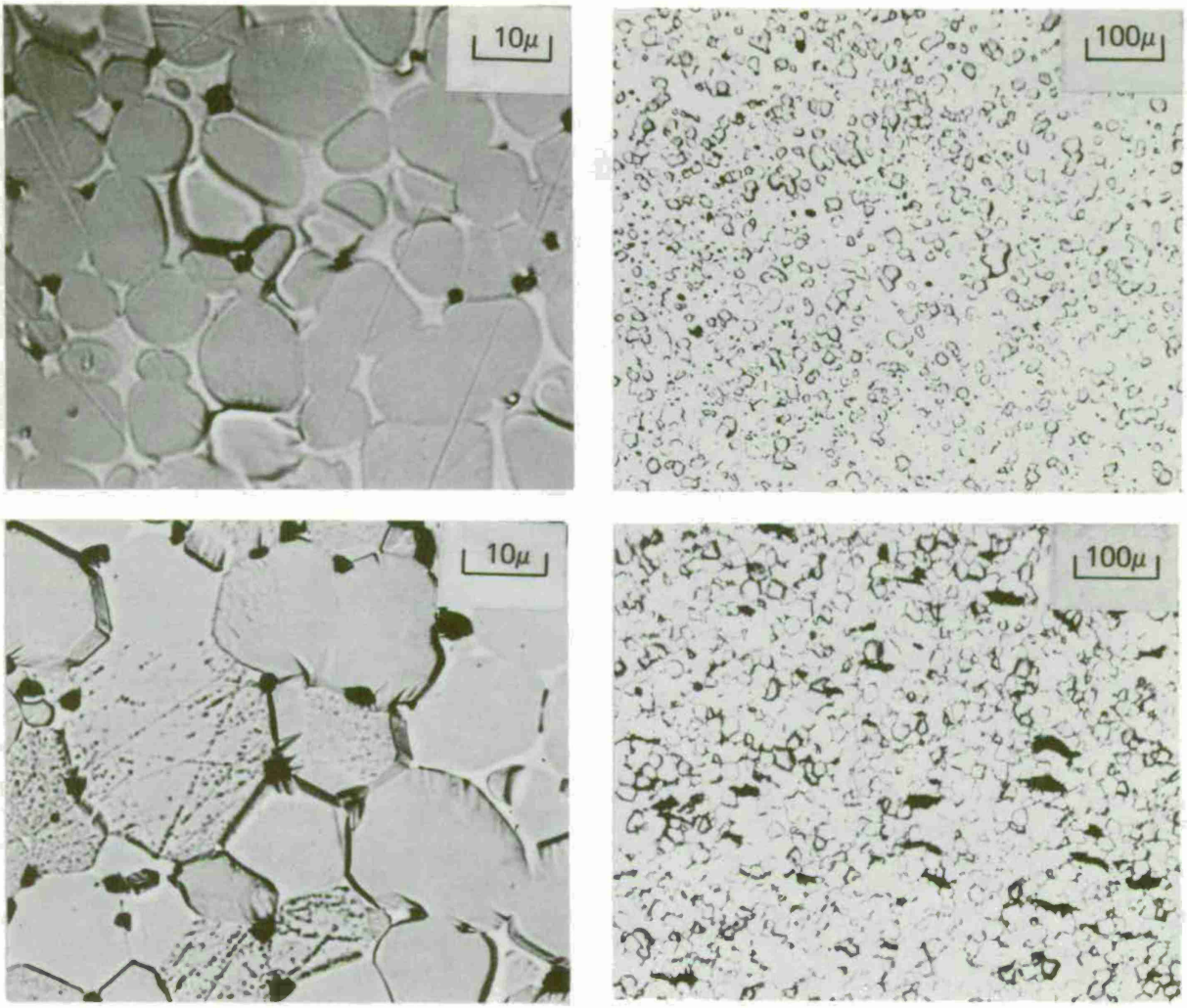

Figure 8. Impulse resistance sintered tungsten-nickel powder mix.
a. 96% W-4% Ni - 98% dense.
b. 98% W-2% Ni - 94% dense.

In spite of the favorable aspects noted, strength of the as-sintered forms (Table 2) appears to reflect premature fracture, probably as the result of residual defects. It is suggested that the fine grain structures that have been demonstrated, free of such apparent defects, should obtain significant advances in strength, and that this condition might be approached by "forge preform" methods.

ACKNOWLEDGMENT

The able assistance of Mr. Walter Jason in die design and equipment operation is greatly appreciated. Previously established background and advice by Dr. Saul Isserow and Dr. Lawrence Shepard were of great assistance in the present effort.

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Technical Report AMMRC TR 76-32, September 1976, 13 pp -
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